

Sorption of isoxaflutole by five different soils varying in physical and chemical properties

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Abstract: Isoxaflutole is a new pre-emergence corn herbicide which controls both grass and broadleaf weeds. Experiments were performed in the laboratory to study the sorption of isoxaflutole in five different soils (Moorhead, MN; East Monroe, CO; Ellendale, MN; South Deerfield, MA; and Chelsea, MI) using the batch equilibration technique. Total initial isoxaflutole solution concentrations for each soil were 0.05, 0.15, 0.3, 0.8, 1.5, 2.0 and 4.0 mg litre⁻¹. Analysis of [*ring*-¹⁴C] isoxaflutole was performed using liquid scintillation counting, and sorption data were fitted with the Freundlich model. Isotherms of isoxaflutole in all the soils were non-linear as depicted by the exponent ($n < 1.0$), indicating differential distribution of sorption site energies in various soils. Since the isotherms were non-linear the data fit Freundlich's isotherm well, as was indicated by high values of the regression coefficient (r^2). The Freundlich sorption coefficient ranged from 0.555 to 50.0 (litreⁿmg¹⁻ⁿkg⁻¹). Multiple regression of the sorption constant, K_F against selected soil properties indicated that organic matter content was the best single predictor of isoxaflutole sorption ($r^2 = 0.999$) followed by soil pH ($r^2 = 0.954$). Clay content of the soils did not have a high correlation with K_F values ($r^2 = 0.453$), while the sorption of isoxaflutole was not influenced by the Ca²⁺ concentration in the soil solution. Isoxaflutole sorption increased with an increase in organic matter content of soils. Sorption of isoxaflutole decreased as the soil pH increased from 4.5 to 8.5, which was depicted by the reduction of K_F values. Sorption of isoxaflutole to the soils varied with differences in binding energies. At a particular net energy value (E^*), the corresponding site energy distribution [$F(E^*)$] values followed the order, Chelsea, MI > Moorhead, MN > East Monroe, CO > South Deerfield, MA > Ellendale, MN. The negative magnitude of Gibbs free energy of sorption (ΔG^x) indicates the spontaneity of the given sorption process in the soils from Moorhead, MN; East Monroe, CO and Chelsea, MI.

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1 INTRODUCTION

Isoxaflutole, [5-cyclopropyl-1,2-oxazol-4 yl α,α,α -trifluoro-2-mesyl-*p*-tolyl ketone], is a new pre-emergence herbicide which belongs to a new class of herbicide, the isoxazoles.¹ Isoxaflutole disrupts pigment biosynthesis via an inhibition of *p*-hydroxyphenyl pyruvate dioxygenase (HPPD) in susceptible plant species.² Isoxaflutole is chemically benzoyl isoxazole and it rapidly converts to a diketetonitrile (DKN) derivative, [(2-mesyl-4-trifluoromethylbenzoyl)-cyclopropylcarbonyl acetonitrile] by opening of the isoxazole ring.³ The conversion to DKN takes place rapidly in plants and soil. In soil, isoxaflutole undergoes rapid conversion to DKN and it is partially sensitive to light. The half-life of isoxaflutole is 20 h in light and 23 h under dark soil photolysis conditions, while the half-life of isoxaflutole is 40 h in light under aqueous photolysis conditions at 25 °C (Chris Leake, Rhône-Poulenc Ag Co per comm)

Isoxaflutole has provided excellent selective control of both grass and broadleaf weeds in corn. It has been

reported to control grasses including barnyard grass [*Echinochloa crus-galli* (L) Beauv], large crabgrass [*Digitaria sanguinalis* (L) Scop] and broadleaf weeds such as velvetleaf (*Abutilon theophrasti* Medic), common redroot pigweed (*Amaranthus retroflexus* L), common ragweed (*Ambrosia artemisiifolia* L), and lambsquarters (*Chenopodium album* L).^{4,5}

Isoxaflutole acts through soil, therefore sorption plays an important role in understanding its fate and behaviour in soil. Soils are heterogeneous systems and they have a tremendous capacity to adsorb chemicals. Sorption reactions offer a major mechanism for the attenuation of environmentally sensitive compounds. Sorption contributes to large-scale processes, as in the transport of chemicals from soil to groundwater, and to microscale processes, as in diffusion and biotransformation. The removal of herbicides from solution by sorption is a major factor controlling herbicide activity, mobility, and persistence.^{6,7}

Most herbicides are solid organic compounds of limited aqueous solubility, are non-ionic in the normal

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Table 1. Physical and chemical properties of the five different soils collected from the Ap horizon (0–15 cm)

Location	Taxonomic class	pH (0.01M CaCl ₂)	Texture	Sand (%)	Silt (%)	Clay (%)	OM ^a (%)	CEC ^b (meq 100g ⁻¹)	Ca ²⁺ (mg litre ⁻¹)
Moorhead, MN	Typic Epiaquet	7.04	Silt clay loam	18	52	30	3.61	33	4700
East Monroe, CO	Aridic Argiustoll	6.55	Clay loam	30	36	34	2.45	17	2216
Ellendale, MN	Typic Hapludoll	6.71	Sandy clay loam	75	15	10	1.76	16	1200
South Deerfield, MA	Typic Udifluent	6.18	Silty loam	27	65	8	1.94	4.9	916
Chelsea, MI	Oxyaquic Hapludalf	5.27	Muck soil	16	41	43	57.4	36	4750

^a Soil organic matter content.^b Cation exchange capacity.

range of soil pH and have low vapour pressures.⁶ For non-ionic, slightly soluble compounds under consideration, a correlation is always found between the amount sorbed by different soils at a given equilibrium concentration and the amount of organic matter present in the soils.⁷ A correlation is usually observed between sorption and soil clay content, but this is regarded as a secondary result, because organic matter and clay are usually correlated between soils.⁶

Before recommending the use of isoxaflutole, studies have to be done to assess the environmental impact of this herbicide. Since it is a pre-emergence herbicide, extensive studies need to be done to observe the fate of isoxaflutole in soil, and the influence of various edaphic factors such as soil pH, organic matter, adsorbed cations, moisture, etc on the sorption of isoxaflutole have to be examined. Preliminary studies on a range of soils in the mid-west region of the United States have shown some injury to crops following pre-emergence application of isoxaflutole (pers comm). Most of these soils were limed each year without proper incorporation into the soil, and the resultant calcium content of some of these soils was therefore very high. Hence there is a speculation about the role of calcium on the sorption of isoxaflutole on these soils.

The objectives of the present study were to: (a) evaluate the effect of organic matter, soil pH, Ca²⁺ concentration, and clay content on the sorption of isoxaflutole and (b) determine the sorptive behaviour of isoxaflutole by five different soils.

2 MATERIALS AND METHODS

Experiments were conducted at the University of Massachusetts with five soils obtained from Moorhead, MN; East Monroe, CO; Ellendale, MN; South Deerfield, MA and Chelsea, MI. The soils were collected from the subsurface horizon (0–15 cm) having a wide variation in their soil texture, pH, organic matter, adsorbed cation (Ca²⁺) and cation exchange capacity (CEC) (Table 1). Soil from South Deerfield, MA was used for detailed studies with various edaphic factors such as soil pH and Ca²⁺ concentrations.

All glassware coming in contact with isoxaflutole was rinsed with 1% hydrochloric acid followed by 1%

ethylenediamine tetra acetic acid (EDTA) solution. Amber-colored glass vials were used in order to reduce photodegradation of isoxaflutole.

Sorption experiments were conducted using a batch equilibration technique in 8-ml screw-cap vials with Teflon[®]-lined septa. An aqueous suspension containing calcium chloride (0.01 M) was used to mimic soil conditions, while mercury (II) chloride (200 mg litre⁻¹) was used as a bioinhibitor and the solution was adjusted to pH 6.7.^{8,9} Wolf *et al*¹⁰ reported that mercury (II) chloride was equivalent to three times autoclaving, yet had little impact on cation exchange capacity, extractable metal ion concentrations, and pH.

A preliminary sorption experiment was conducted for each soil to: (i) determine an appropriate solid/solution ratio for the more detailed subsequent sorption experiments and (ii) determine contact times required to attain sorption equilibria. Based on the results of these preliminary studies, a fixed solid/solution ratio designed to achieve 30–65% reduction in aqueous-phase solute concentrations during sorption was calculated. The solid/solution ratios for the soils were based on their organic matter contents. The solid/solution ratios were 0.50, 0.54, 0.85, 0.88, and 0.03 for the soils from Moorhead, MN; East Monroe, CO; Ellendale, MN; South Deerfield, MA; and Chelsea, MI, respectively. Two blanks without soils were run for each initial concentration. Duplicate soil samples were used according to the predetermined solid/solution ratios of the five different soils and the experiments were repeated twice.

[ring-¹⁴C]Isoxaflutole (99.3%) and technical grade isoxaflutole (98.0%) were obtained from Rhône-Poulenc Secteur Ag Co (14–20 Rue Pierre Baizet B P 9163, 69263 Lyon Cedex 09, France). Radiolabeled isoxaflutole was added to non-radioactive solutions to give the required initial concentrations (≈ 5000 DPM ml⁻¹). The specific activity of the [¹⁴C]isoxaflutole was 18.35 mCi mmol⁻¹. Suspensions were shaken mechanically at 25(±2)°C in 8-ml amber-colored glass vials in hematology mixers (Fisher Scientific Co) giving rocking-rotating motions for 12 h. The aqueous solubility of isoxaflutole is 6.2 mg litre⁻¹ and hence a concentration range of 0.05 to 4 mg litre⁻¹ of isoxaflutole was used. Total initial isoxaflutole concentrations for each soil were 0.05,

Table 2. Sorption coefficients (K_F), slope (n) and regression coefficients (r^2) of isoxaflutole sorption by different soils

Location	n ($\pm SE$)	K_F [$\text{litre}^n \text{mg}^{1-n} \text{kg}^{-1}$]	$\log K_F$ ($\pm 95\% \text{ CI}$)	r^2
Moorhead, MN	0.998 (± 0.008)	2.655	0.424 (± 0.006)	0.996
East Monroe, CO	0.978 (± 0.008)	1.026	0.011 (± 0.006)	0.999
Ellendale, MN	0.967 (± 0.011)	0.555	-0.256 (± 0.008)	0.999
South Deerfield, MA	0.930 (± 0.008)	0.646	-0.190 (± 0.006)	0.999
Chelsea, MI	0.954 (± 0.008)	50.00	1.699 (± 0.007)	0.999

0.15, 0.3, 0.8, 1.5, 2.0 and 4.0 mg litre⁻¹. After mixing, the vials were centrifuged at 900g for 15 min and supernatants were sampled. Aliquots (1 ml) of the clear supernatants were mixed with 12 ml of Scintiverse[®] scintillation cocktail (Fisher Scientific Co), and the amount of radioactivity was determined by liquid scintillation counting in an LS 3801 analyzer (Beckman Instruments)

Since there was no biodegradation and little sorption by vials, isoxaflutole sorbed by soil samples was calculated by mass difference. The amount of isoxaflutole sorbed to the soil after equilibration was calculated from the difference between the initial and equilibrium solution concentration. Isotherms were constructed for all five soils and data were fitted to Freundlich's model,

$$x/m = K_F C_e^n$$

and the log-transformed form,

$$\log[x/m] = \log K_F + n \log C_e$$

where x/m is the sorbed concentration (mg kg⁻¹), C_e is the equilibrium concentration of sorbate (mg litre⁻¹), K_F is the Freundlich coefficient (litre ^{n} mg ^{$1-n$} kg⁻¹) and n (dimensionless) is a constant. Although this expression is empirical, n reflects the curvature in the isotherm and may be taken to represent the energy distribution of sorption sites.^{11,12}

The parameters K_F and n were determined by linear regression of log-transformed data. Linear fit of log-transformed data was justified over direct non-linear curve fitting as the concentrations were spread evenly over the log-scale, thus non-linear curve fitting would underestimate the importance of the low concentration data.¹³

In order to study the effect of pH on the sorption of isoxaflutole, experiments were conducted at pH 4.5, 5.5, 6.5, 7.5 and 8.5 with the South Deerfield soil. Because South Deerfield, MA soil had a normal pH of 6.5 the soil was incubated in the laboratory until it reached the required pH. For studies with Ca²⁺, the experiments were conducted at 0.01 M and 0.1 M Calcium chloride concentrations.

3 RESULTS AND DISCUSSION

3.1 Sorption of isoxaflutole

Sorption isotherms of isoxaflutole in all the soils were non-linear, as depicted by the exponent ($n < 1.0$),

indicating differential distribution of sorption site energies in various soils. Since the isotherms were non-linear the data fit Freundlich's isotherm well, as was indicated by high values of the regression coefficient ($r^2 = 0.996$ to 0.999) (Table 2). This is because the Freundlich equation, although originally empirical, implies that the affinity for sorption decreases exponentially with increasing solution concentration, which is closer to reality.^{14,15} Values of n were close to unity in all soils, suggesting partitioning as a dominant adsorption mechanism. Hence, it was possible to compare the K_F values and determine the comparative sorption capacities of the soils. Similar n values have been observed for other herbicides like flumetsulam 2',6'-difluoro-5-methyl[1,2,4]triazolo-[1,5-*a*]pyrimidine-2-sulfonamide across a wide range of soil types.¹⁶ The K_F values suggest that isoxaflutole was strongly sorbed to the soil from Chelsea, MI [50 litre^{0.954} mg^{0.046} kg⁻¹] followed by Moorhead, MN;

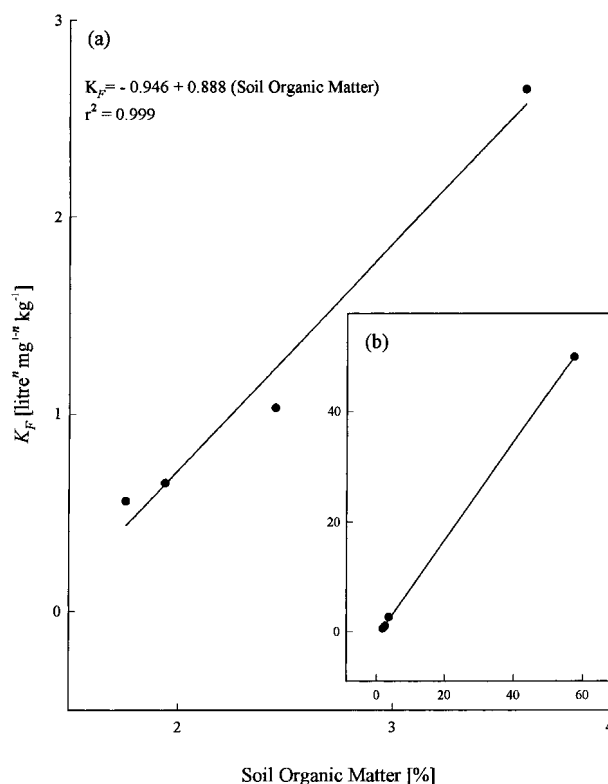


Figure 1. Freundlich sorption coefficient (K_F) as influenced by soil organic matter in (a) Moorhead, MN; East Monroe, CO; Ellendale, MN; and South Deerfield soils and (b) all five soils including Chelsea, MI soil. Points are observed values while the line is fit to a linear regression model.

East Monroe, CO; South Deerfield, MA; and Ellendale, MN.

3.2 Effect of organic matter

A positive correlation between soil organic matter content and isoxaflutole sorption was observed. Regression between K_F values and soil organic matter ($r^2=0.999$) indicated that isoxaflutole sorption increased with an increase in organic matter content of soils as shown in Fig 1(b). A similar effect of organic matter content on the sorption of atrazine {6-chloro- N^2 -ethyl- N^4 -isopropyl-1,3,5-triazine-2,4-diamine} and flumetsulam has been reported.^{7,18} Chiou¹⁹ has reported that soil organic matter is the primary sorbent for hydrophobic organic compounds in soil and isoxaflutole falls in the same category. However, isotherm non-linearity of isoxaflutole in soils having high organic matter content cannot be attributed to mineral surface, but can be attributed to the characteristic of soil organic matter. Non-linear isotherms for atrazine and chlorinated benzenes have been reported.^{9,20}

In studying the sorption of hydrophobic organic compounds, the quantity as well as the type of organic matter is important.²² Soil organic matter is heterogeneous in nature and can vary greatly as a function of the age, diagenesis, and mode of transformation.^{22,23} The variation in quality of soil organic matter strongly affects the sorption capacity of hydrophobic organic compounds.^{8,12}

3.3 Effect of clay content

The effect of clay content on the sorption of imidacloprid, [1-(6-chloro-3-pyridylmethyl)- N -nitroimidazolidin-2-ylideneamine] has been reported. By Cox *et al.*,²⁴ who found a contribution of the surfaces of mineral components of the soil clay to sorption. Montmorillonitic clay minerals were found to be active in the sorption of imidacloprid. Laird *et al.*²⁵ reported that smectites influence the sorption behavior of atrazine and the affinity of smectites for atrazine decreases with increasing surface charge density. In our study, the sorption of isoxaflutole was not influenced appreciably by clay content, as depicted by a low regression coefficient ($r^2=0.453$). Sorption, persistence and mobility of isoxaflutole in soils containing 2% or more organic matter were found to be correlated with soil organic matter content and not with the soil texture, which is consistent with our results.²⁶

In soil, clay and organic components are usually intimately associated, such that their individual effects on sorption are difficult to separate. However, mineral surfaces may be obscured by their association with organic colloids. Sorption of imidacloprid on soil clays decreased after removal of organic matter.²⁴ Sorption of isoxaflutole in soils was found to be influenced primarily by organic matter, while clay components did not greatly affect the sorption process.

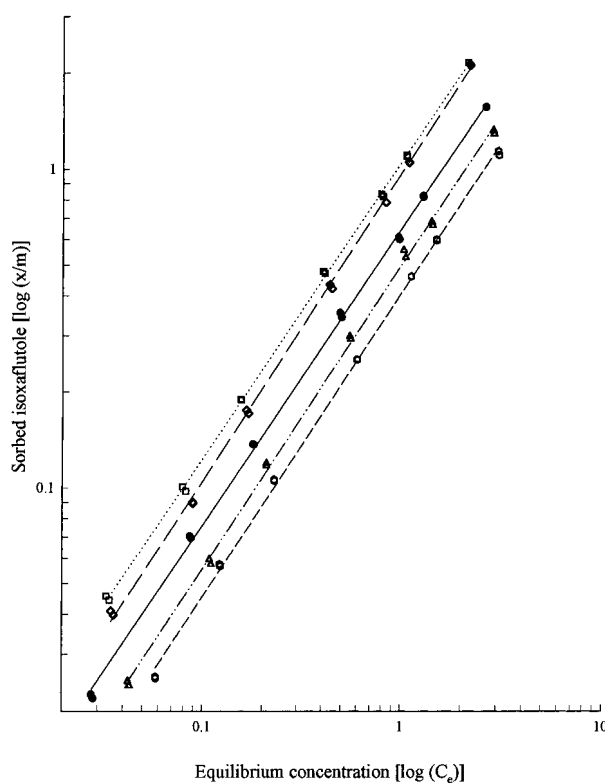


Figure 2. Freundlich sorption isotherms of isoxaflutole in South Deerfield, MA soil at pH (□) 4.5, (◇) 5.5, (●) 6.5, (△) 7.5, and (○) 8.5. Data points are duplicate observations at each concentration, while the lines are fit to linear regression, x/m indicates the amount of isoxaflutole adsorbed by unit weight of soil (mg kg^{-1}) and C_e denotes the equilibrium concentration (mg litre^{-1}).

3.4 Effect of Ca^{2+} concentration

The effect of Ca on sorption of isoxaflutole was investigated with soils from South Deerfield, MA and Chelsea, MI. These soils had the lowest (916 mg kg^{-1}) and the highest (4750 mg kg^{-1}) Ca^{2+} concentrations, respectively. South Deerfield, MA soil had 1.94% organic matter compared to 57.4% in the Chelsea, MI soil. In the South Deerfield soil K_F increased by $0.068 \text{ litre}^n \text{ mg}^{1-n} \text{ kg}^{-1}$ as the concentration increased from 0.01 M to 0.1 M calcium chloride indicating that the availability of isoxaflutole in the soil solution decreased as the Ca^{2+} concentration increased. Sorption of isoxaflutole in Chelsea, MI soil was not influenced by Ca^{2+} concentration, as reflected by a negligible change in the K_F and n values. Hence the effect of Ca^{2+} concentration on the sorption of isoxaflutole could be ruled out and the injury to plants can not be accounted for by Ca^{2+} concentrations.

3.5 Effect of soil pH

Soil pH and organic matter content are important factors governing the sorption of herbicides.^{16,27} Experiments were performed with South Deerfield, MA soil to study the effect of soil pH on the sorption of isoxaflutole. The soil had a normal pH of 6.5 in a 1:1 ratio with water and, hence, the soil was incubated with 0.01 M calcium chloride and $200 \text{ mg litre}^{-1}$

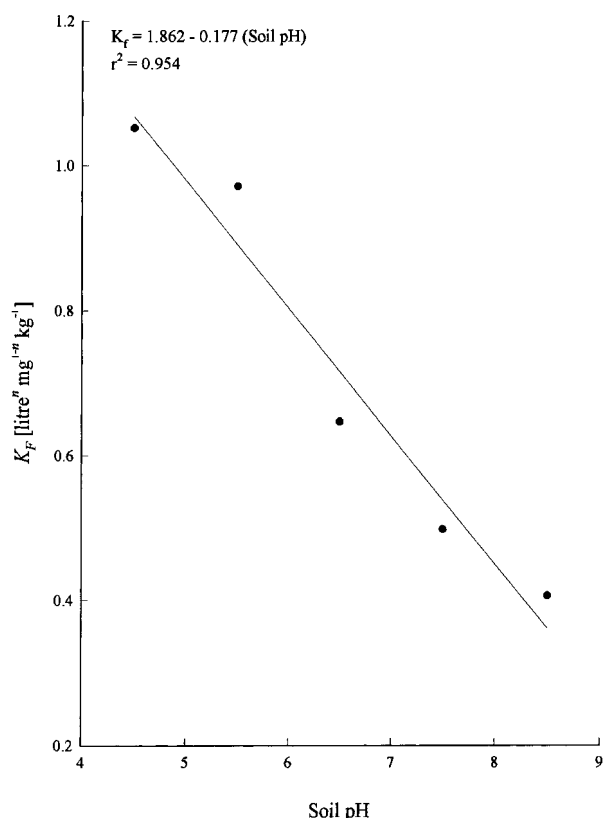


Figure 3. Freundlich sorption coefficient (K_F) as influenced by soil pH in South Deerfield, MA soil. Points are observed values while the line is fit to a linear regression model.

mercury (II) chloride until the soil reached the required pH. The background solution of 0.01M calcium chloride and 200mg litre⁻¹ mercury (II) chloride had a pH of 6.7 but it was not buffered, so the solution actually attained the same pH as the soil. Isotherms were constructed at pH 4.5, 5.5, 6.5, 7.5, and 8.5 (Fig 2).

A negative correlation ($r^2=0.954$) was observed between K_F and soil pH (Fig 3). Isoxaflutole sorption decreased as the soil pH increased from 4.5 to 8.5 which was demonstrated by the reduction in K_F values (Table 3). The fact that isoxaflutole binds strongly to the soil at lower pH may be due to the low basicity of the isoxazole ring which enables proton addition to isoxaflutole at low soil pH.²⁶ Hence sorption of isoxaflutole by cation exchange is higher at low soil pH than in soils at high pH. Rouchaud *et al*²⁶ have reported that isoxaflutole dissipation in soils is slightly faster at pH 7.2 than at 5.5, which is similar to our

observation for sorption of isoxaflutole in soils with low pH. It is possible that at pH 8.5 some of the organic matter dissolves in the solution and this may contribute to the reduction of K_F value. Similar findings have been reported by Huang and Weber²⁸ where they observed background dissolved organic matter at pH < 7.0.

Shaw and Murphy¹⁸ reported that flumetsulam mobility across soils with similar organic matter content increased linearly as soil pH increased from 5.3 to 7.2. They attributed the increased mobility of flumetsulam to its ionic species at pH ≥ 7.2 . Therefore, like many other herbicides, isoxaflutole sorption depends on organic matter content and soil pH. When isoxaflutole is being recommended for soils having low organic matter and high pH it may be necessary to reduce the application rate. Sorption of isoxaflutole is higher in soils having high organic matter content and low pH, compared to soils with low organic matter and high pH. Hence the chances of injury are lesser in soils with high organic matter content and low pH as the amount of available isoxaflutole in soil solution will be reduced.

3.6 Site energy distribution

The sorption isotherms for all soils were non-linear ($n < 1.0$) and hence, the data did not fit the Langmuir model well but they fit the Freundlich model well as indicated by the high regression coefficients ($r^2 = 0.996$ to 0.999) (Table 2). In many isotherm models, there is an implicit assumption of an underlying distribution of site energies. On a theoretical basis, isotherm parameters can thus be related to particular site energy distributions, and their empirically determined values can be interpreted with respect to the energy characteristic of a sorbent.²⁹ The basic integral equation underlying the theory of heterogeneous surfaces is;

$$Q_e(C_e) = \int qh(E, C_e)F(E)dE$$

where Q_e defines the total sorption of a solute by a heterogeneous surface as the integral of an energetically homogenous isotherm (qh), multiplied by a site energy frequency distribution [$F(E)$] over a range of energies, C_e the equilibrium concentration of the solute, and E is the difference between the solute and solvent adsorption energies for a given site.²⁹ While the limits on the integral are most appropriately based on the minimum and maximum adsorption energies

Table 3. Sorption coefficients (K_F), slope (n) and regression coefficients (r^2) of isoxaflutole on South Deerfield, MA soil incubated for three weeks in order to obtain the required pH

pH	n ($\pm SE$)	K_F [litre ⁿ mg ¹⁻ⁿ kg ⁻¹]	$\log K_F$ ($\pm 95\% CI$)	r^2
4.5	0.931(± 0.006)	1.052	0.022(± 0.005)	0.999
5.5	0.967(± 0.008)	0.971	-0.013(± 0.006)	0.999
6.5	0.930(± 0.008)	0.646	-0.190(± 0.006)	0.999
7.5	0.952(± 0.009)	0.498	-0.303(± 0.007)	0.999
8.5	0.952(± 0.009)	0.406	-0.391(± 0.006)	0.999

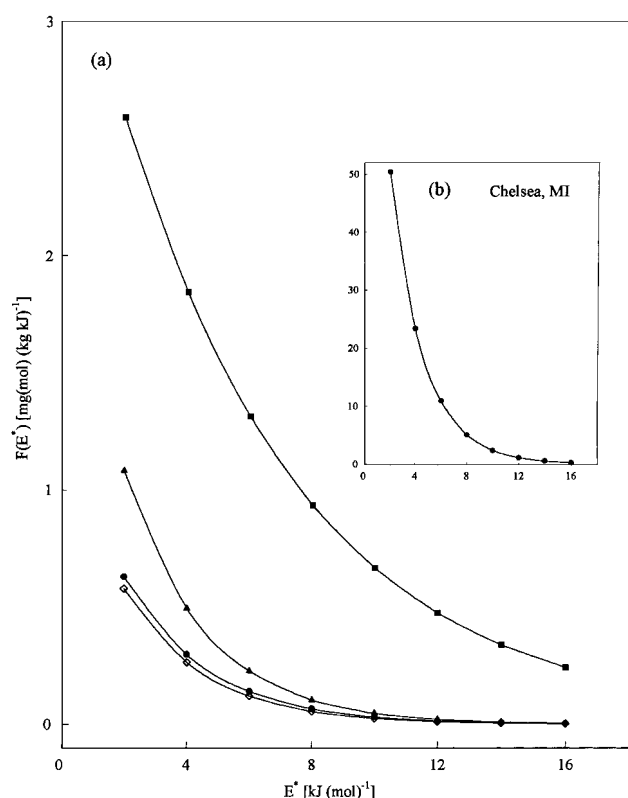


Figure 4. Site energy distribution for isoxaflutole sorption on (a) (■) Moorhead, MN; (▲) East Monroe, CO; (◇) Ellendale, MN; and (●) South Deerfield, MA soils and (b) Chelsea, MI soil. Points are mean observed values.

which are generally assumed for convenience, they range from zero to infinity.^{30,31}

Cerofolini³² proposed a technique for the determination of site energy distributions in which the equilibrium liquid phase concentration is related to the energy of adsorption by

$$C_e = C_s \exp \frac{-(E - E_s)}{RT}$$

$$C_e = C_s \exp \frac{-[E^*]}{RT}$$

where E^* is the net energy, C_e the equilibrium concentration of the solute, C_s the maximum solubility of the solute, E the difference between the solute and solvent adsorption energies for a given site, E_s that value of the sorption energy corresponding to $C_e = C_s$, R the universal gas constant, and T is the absolute temperature. The E_s reference state for E represents

the lowest physically realizable sorption energy, and its magnitude depends only on the solute, or in other words it is independent of the sorbent. The parameter E_s is analogous to E_o in that it determines the position of the distribution on the energy axis.²⁹

The approximate site energy distribution, $F(E^*)$, is obtained by differentiating $q_e(E^*)$, with respect to E^* .

$$F(E^*) = \frac{-dq_e(E^*)}{dE^*}$$

For Freundlich isotherms;

$$F(E^*) = \frac{K_F C_s^n n}{RT} \cdot \exp [-nE^*/RT]$$

The equilibrium concentrations used in the experiments ranged from 0.02 to 2.07 mg litre⁻¹. Using the above equation the energy of adsorption ranged from 2.7 to 14.2 kJ mol⁻¹. The energy distribution of isoxaflutole in various soils is represented in Fig 4. Isoxaflutole was sorbed strongly by the Chelsea, MI soil, as indicated by the energy distribution in Fig 4(b). The site energy distribution curves emphasize the fact that isoxaflutole binds tightly to soils with higher organic matter content as the curves illustrate. At a particular E^* value, the corresponding $F(E^*)$ values follow the order Chelsea, MI > Moorhead, MN > East Monroe, CO > South Deerfield, MA > Ellendale, MN. The trend is represented by the individual organic matter contents of the soils.

3.7 Thermodynamic calculations

Biggar and Cheung³³ studied the sorption of carboxylate pesticides in soils. They regarded it as a process of partitioning between the bulk solution phase and a surface phase.³⁴ In our studies the sorption of isoxaflutole was primarily a partitioning process as depicted by the n values in all soils (Table 2). This partition process can be characterized by a distribution coefficient (K_o) given by the following equation.³⁴

$$K_o = a_s/a_e = \gamma_s C_s / \gamma_e C_e$$

where a_s indicates the activity of the sorbed solute, a_e is the activity of the solute in the equilibrium solution, γ_s is the activity coefficient of the sorbed solute, γ_e is the activity coefficient of the solute in the equilibrium solution, C_e is the amount of solute sorbed and C_s is the equilibrium solute concentration. It is assumed that K_o is related to the standard differential Gibbs free energy of sorption (ΔG^x) in the limit of infinitely dilute

Table 4. Free energy for isoxaflutole sorption (ΔG^x), sorption coefficient ($\log K_F$), and distribution coefficient ($\ln K_o$) at 25 °C

Soil sample	$\log K_F$ (±95%CI)	$\ln K_o$	ΔG^x (kJ mol ⁻¹)
Moorhead, MN	0.424 (±0.006)	1.037	-2.568
East Monroe, CO	0.011 (±0.006)	0.086	-0.213
Ellendale, MN	-0.256 (±0.008)	-0.431	1.067
South Deerfield, MA	-0.190 (±0.006)	-0.117	0.290
Chelsea, MI	1.699 (±0.007)	4.078	-10.10

sorption solution.¹⁵ Thus,

$$\lim_{C_s \rightarrow 0} \frac{C_s}{C_e} = K_o$$

when the γ_s terms approach unity, and

$$(\Delta G^x) = -RT \ln K_o$$

The value of K_o was obtained by plotting $\ln(C_s/C_e)$ vs C_s , and then extrapolating to zero C_s . The value of K_o was determined by the intercept.¹⁵

The experiments were conducted at 25 °C so the free energy was calculated at the same temperature. Negative ΔG^x values indicate the spontaneity of the given sorption process in the soils from Moorhead, MN; East Monroe, CO and Chelsea, MI (Table 4). The soils with comparatively higher organic matter content and higher K_F values depicted a spontaneous process.

4 CONCLUSION

Isoxaflutole can be used as a pre-emergence herbicide to selectively control grasses and broadleaf weeds in corn. Sorption isotherms of isoxaflutole in all soils were non-linear as depicted by the exponent ($n < 1.0$), indicating differential distribution of sorption site energies in various soils. Since the isotherms were non-linear, the data fit Freundlich's isotherm well as was indicated by high values of the regression coefficient.

Isoxaflutole sorption increased with increase in the organic matter content of the soils. Soil organic matter content was the best single predictor of isoxaflutole sorption ($r^2 = 0.999$) followed by soil pH ($r^2 = 0.954$). Sorption of isoxaflutole decreased as the soil pH increased from 4.5 to 8.5, which was depicted by the reduction of K_F values. Clay content and Ca^{2+} concentration of the soils did not greatly affect the sorption of isoxaflutole. The site energy distribution calculations emphasize the fact that isoxaflutole binds tightly to soils with higher organic matter content. At a particular E^* value, the corresponding $F(E^*)$ values follow the order Chelsea, MI > Moorhead, MN > East Monroe, CO > South Deerfield, MA > Ellendale, MN. The trend is represented by individual organic matter contents of the soils.

The portion of isoxaflutole in soil solution will determine crop injury, leaching potential and, subsequently, chances of contamination of ground water. Sorption of isoxaflutole is higher in soils having high organic matter content and low soil pH and hence the amount of available isoxaflutole in soil solution will be less. Chances of crop injury are less in soils with high organic matter and low soil pH, compared to soils with low organic matter and high soil pH. We are currently studying the sorption and desorption of DKN which will give us a complete idea about the fate of isoxaflutole and its derivatives in soil.

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